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Phase Separation of Liquid Crystals in Polymers

by

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PHASE SEPARATION OF LIQUID CRYSTALS IN POLYMERS

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Abstract New optoelectronic materials based on polymer dispersed liquid crystals (PDLC) show great potential for application in displays, temperature sensors, optical computing and for solar energy control. We report liquid crystal, thermoset or thermoplastic materials. PDLC materials may be formed by several different processes. The liquid crystal may be dissolved in low molecular weight polymer precursors, in a thermoplastic melt or with a thermoplastic in a common solvent. Subsequent polymerization, cooling of the polymer melt or solvent evaporation lead to liquid crystal immiscibility, droplet formation and growth, and polymer gelation. The optoelectronic properties of these materials are affected by the droplet morphology. Specific examples are presented for each of these processes and it is demonstrated how the droplet morphology and density, and thus device performance, can be controlled by each method. The thermoplastics are suitable for forming films by a variety of techniques. A range of polymers and liquid crystals may be used to form PDLC materials, allowing them to be tailored for any of a number of applications.



INTRODUCTION

Polymer dispersed liquid crystals (PDLCs) have recently been reported.¹ These materials are formed by the incorporation of liquid crystals in a crosslinked epoxy binder or in a UV cured polymer matrix.^{2,3} The materials may be switched from a scattering to a clear state by application of an electric field. These materials show great promise in a variety of display

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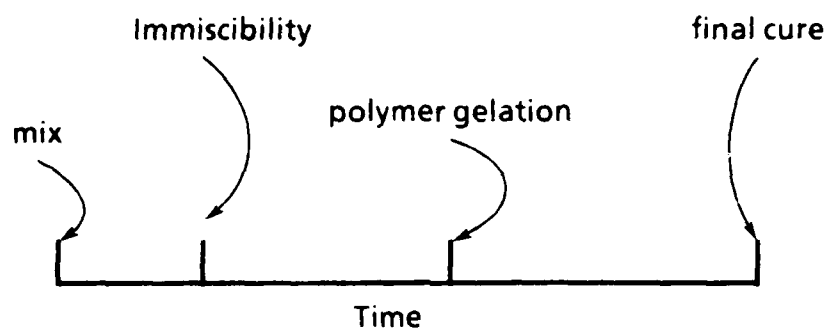


FIGURE 2

Schematic representation of the PIPS process.

the liquid crystal droplets. The polymerization process continues and the liquid crystal within the droplets is purified. Purification of the liquid crystal within the droplets results in an increase in the nematic-to-isotropic phase transition temperature. The refractive index of the liquid crystal in its isotropic phase is more closely matched with the polymer than in the randomly oriented nematic phase. Thus, the film shows a large decrease in the intensity of scattered light at the nematic to isotropic phase transition offering an excellent means of monitoring this transition. The purification of the liquid crystal within the droplets may be due to slow transfer of lower molecular weight oligomers dissolved in the liquid crystal to the polymer binder where they react, lengthening the epoxy chains. The nematic-to-isotropic phase transition becomes narrower and

approaches the temperature of the bulk liquid crystal as the polymerization continues, indicating that the composition of the liquid crystal within the droplets is essentially the same as that of the bulk.

The droplet size and density for materials formed by the PIPS process are highly dependent on the cure temperature. Figure 3

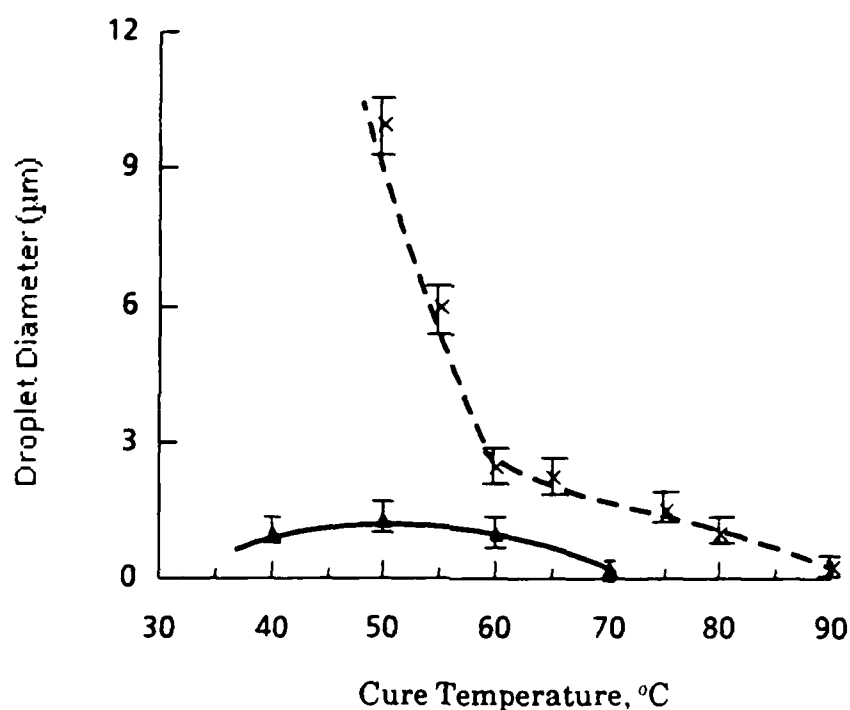


FIGURE 3

Graph of average droplet diameter as a function of cure temperature for: — 1:1:1 mixture of epon 828, capcure 3800 and E7: - - - 20%MK-107, 11% epon 828, 28% capcure 3-800 and 41%E7.

The *t*-butylamine was used to cure the epon because of the low melt temperature of the resulting polymer, $<100^{\circ}\text{C}$. Cooling of the mixture results in phase separation, droplet formation and growth, and polymer gelation. Figure 4 is the phase diagram of E7 in the *t*-butylamine cured Epon. The phase separation temperature was determined as the temperature at which an increase in the light scattered by the material occurred. The intensity of the scattered light was monitored as a decrease in the light transmitted through the material. Figure 5 shows the intensity of light transmitted through samples of various composition as a function of temperature. The polymer is the continuous phase even for relatively high E7 concentrations. Only for E7 concentrations greater than 80% is a continuous liquid crystal phase observed. The polymer has a finite solubility in the liquid crystal and is observed as a depression in the nematic-to-isotropic phase transition temperature for high E7 concentrations.

The rate of cooling of the polymer melt affects the resulting droplet morphology. Figure 6 is a plot of the average droplet diameter *vs* the rate of cooling. Rapid cooling results in smaller droplets and more liquid crystal remaining in the binder. Slower cooling results in larger droplets. This is because slower cooling allows more time for phase separation, droplet growth, and droplet coalescence. The droplet size and density has a major influence on the optoelectronic response of these materials and on the scattering efficiency of these films.^{6,7} The scattering efficiency of the PDLC films is maximized when the droplet size is on the order of the wavelength of light. The driving voltage increases and the turn off time decreases with decreasing droplet diameter. Therefore, the cooling rate of thermoplastic PDLC materials offers an excellent means of controlling device performance.

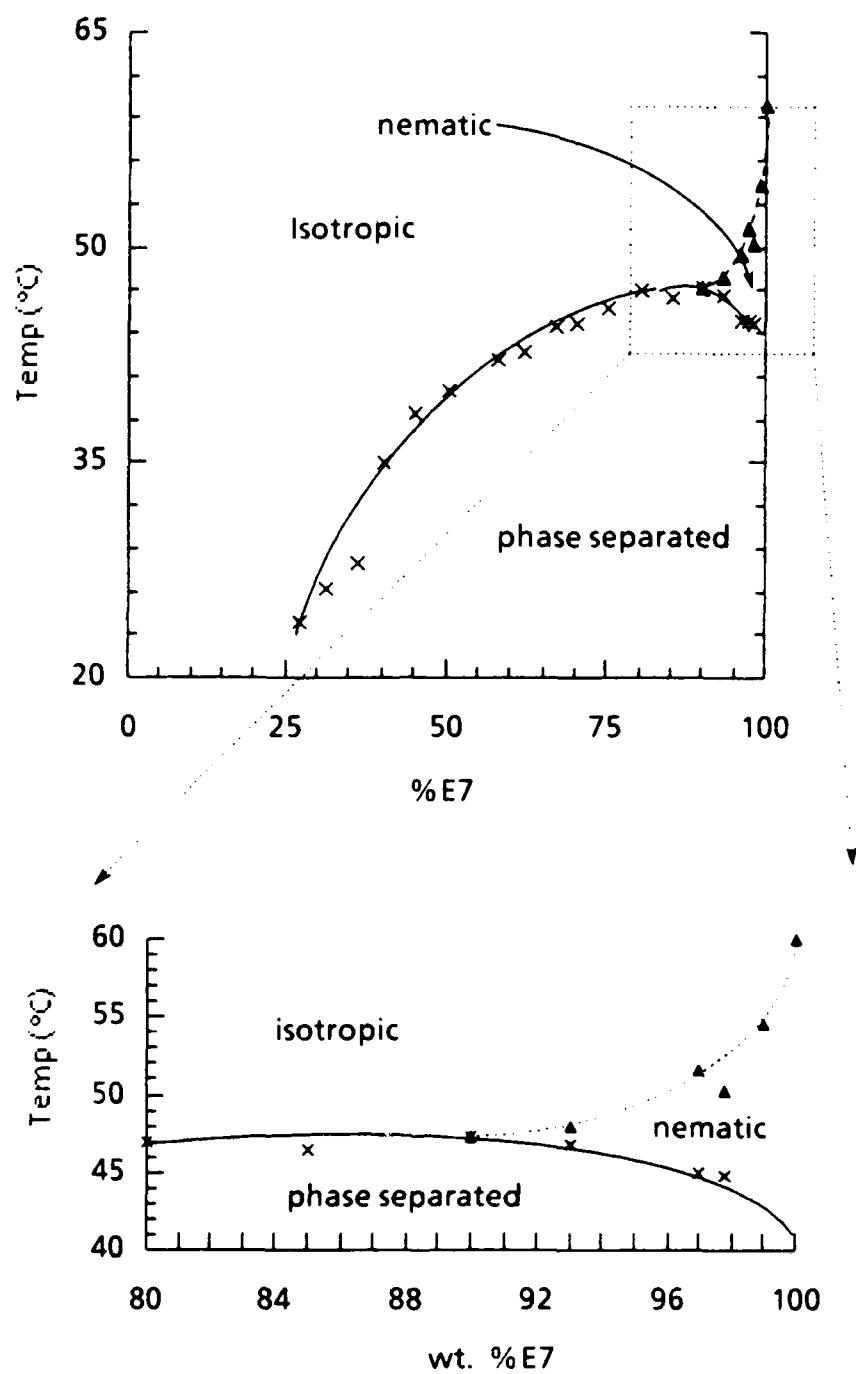


FIGURE 4

Phase diagram of E7 and *t*-butylamine cured Epon 828:

— = droplet formation; = nematic-isotropic transition.

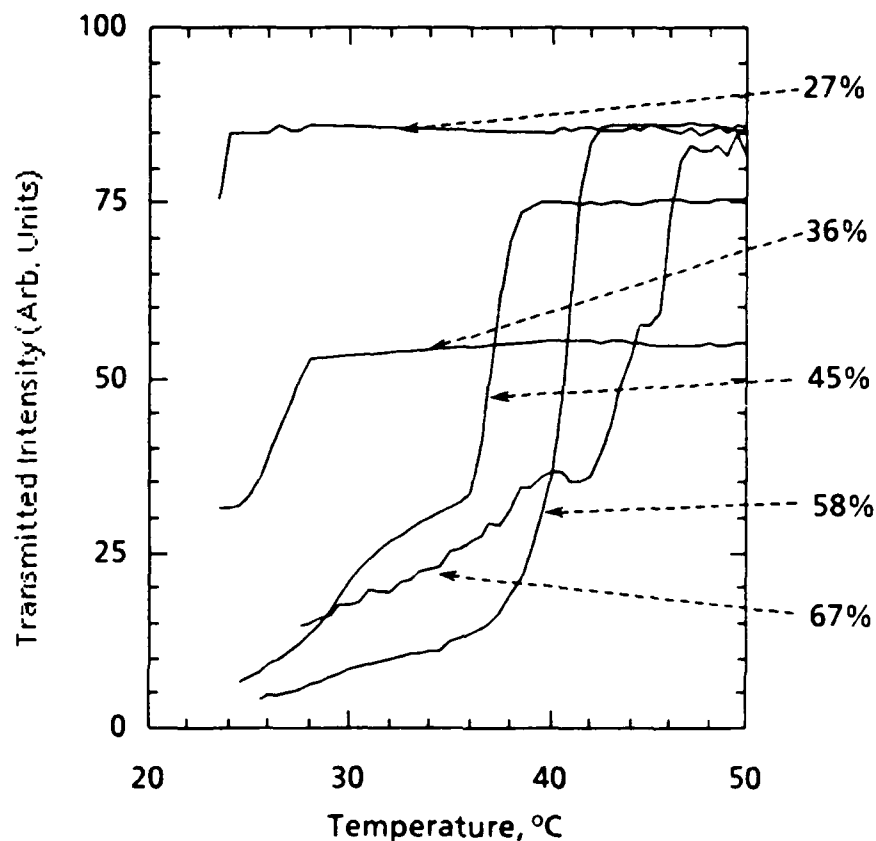


FIGURE 5

Relative transmission vs temperature for films of varying liquid crystal composition in a *t*-butylamine cured Epon 828.

SIPS results when the solvent is removed from a liquid crystal and thermoplastic solution dissolved in a common solvent. Figure 7 is a ternary phase diagram showing schematically the SIPS process. A system consisting of polymer, liquid crystal, and a common solvent of composition represented by point X is made. Evaporation of the solvent moves the system

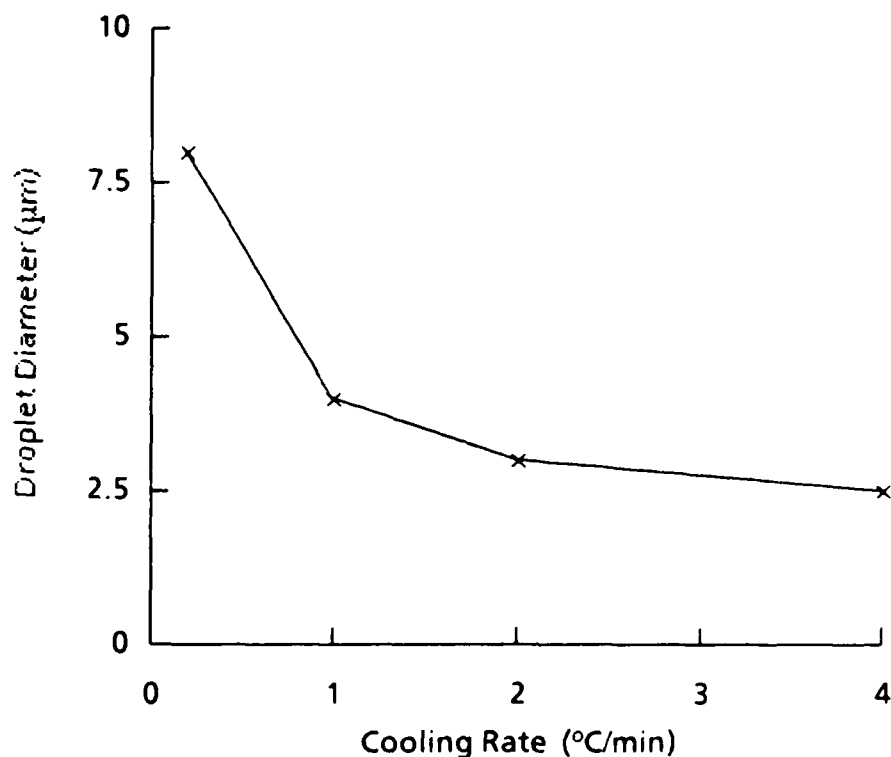


Figure 6

Droplet diameter vs the rate of cooling of a thermoplastic melt consisting of E7 dissolved in Epon 828 cured with *t*-butylamine.

along the line XA. Upon crossing the miscibility gap droplets will form and grow until gelation of the polymer. Point A represents the final composition of the SIPS formed PDLC film. E7 and polymethylmethacrylate (PMMA), dissolved in chloroform were used to form PDLC films by the SIPS process. Evaporation of the chloroform results in the system crossing the miscibility gap, leading to droplet formation and growth and polymer gelation. The droplet size and density are controlled by

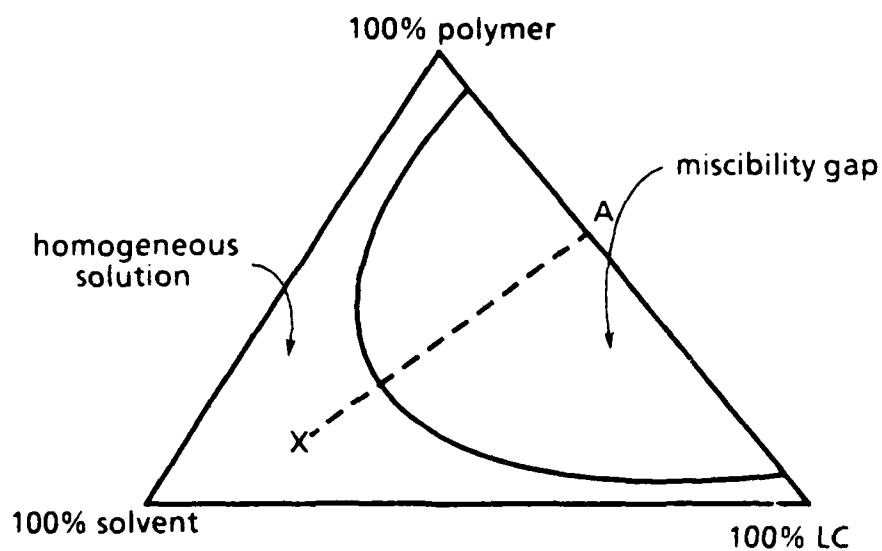


FIGURE 7

Schematic ternary phase diagram of the SIPS process.

the rate of solvent removal. The rate of solvent removal is controlled by the rate at which air is passed over the sample; the faster the air flow rate, the faster the rate of evaporation. Table 1 lists the time to droplet formation and the droplet size as a function of the air flow rate; the slower the air flow rate, and thus the rate of solvent evaporation, the larger the droplet size.

FILM FORMING TECHNIQUES

Thermoplastic PDLC materials may be formed into films by a variety of standard film forming techniques. Solvent coating techniques such as dip coating, doctor blading and wire-wound

Table 1. Droplet Size and Formation Time

Air Flow Rate (ml/min)	Time to Droplet Formation (min)	Droplet Size (μm)
100	34	≤ 1
20	150	3
3	720	12

rods have been used to form uniform films on plastic substrates. Hot melt techniques may also be used with thermoplastic films not containing solvent. The resulting films may be laminated using heat and pressure to form a PDLC film sandwiched between conducting plastic substrates. Draw-down coaters may be used to form films of thermoset PDLC materials. Large area films are possible as are continuous film-forming processes commonly used in plastic film manufacture.

CONCLUSION

PDLC materials may be formed by three basic processes: PIPS, TIPS, and SIPS. Each process involves phase separation of liquid crystals from a homogeneous polymer solution. The droplet size and shape and thus the performance characteristics of the material may be determined by controlling the phase separation process. PDLC films may be made by a variety of standard film forming techniques. They are suitable for a wide variety of

applications, including large area displays, projection displays, solar energy control, and thermometers.

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